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(54) **Barrier materials useful for packaging.**

(57) Improvements to silicon oxide coatings on polymeric substrates are disclosed, which provide improved barrier properties. One improvement involves doping an SiO<sub>2</sub> coating with one or more of certain metals. Another improvement involves first, forming an SiO coating on the substrate, followed by an SiO<sub>2</sub> coating. Another improvement involves the combination of the SiO/SiO<sub>2</sub> coatings plus the incorporation of certain metal dopant into the SiO<sub>2</sub> layer.

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## FIELD OF THE INVENTION

This invention relates to polymeric films having improved barrier properties towards oxygen and other materials.

## Description of Related Art

Flexible polymer films have been used extensively in the packaging of food, electronic and medical products. It is desirable in many applications to have a good barrier to oxygen and/or water vapor. However, most polymer based barrier resins such as ethylene vinyl alcohol copolymer ("EVOH") or polyvinylidene chloride ("PVDC"), although exhibiting good barriers to oxygen or moisture, do so only under ideal conditions. Although EVOH can be an excellent oxygen barrier, it loses its barrier property at moderate to high relative humidity. Thus this material is not widely usable in applications involving high water vapor content, such as moist foods. Although PVDC exhibits good moisture and oxygen barrier properties, it is not suitable for many applications, has an undesirable yellow color, and is difficult if not impossible to recycle. Other proposed alternatives to provide oxygen and water vapor barriers include laminations of aluminum foil and aluminum metallized film. Although these exhibit good barrier properties, they are completely opaque, cannot be recycled, and cannot be readily used for food packaging destined for use in a microwave oven.

U.S. Pat. 3,442,686 discloses multilayer structures as flexible transparent packaging film having good barrier properties to gases and liquids, comprising a flexible transparent organic polymeric base film having thereon an adherent, transparent, flexible highly gas- and liquid-impermeable, moisture resistant, continuous glassy coating of inorganic material, and a sealable, flexible, transparent top coating of organic polymeric material. The glassy coating is sandwiched between the base film and top coating. The preferred base films disclosed include polyester films such as Mylar® oriented, heat set polyester film. The preferred glassy coatings disclosed are the oxides of silicon and aluminum, and the coating thickness is disclosed to be 0.02 to 2 microns (20 to 2000 nm). Among the silicon oxides disclosed are silicon monoxide (SiO) and silicon dioxide (SiO<sub>2</sub>). The glassy coating is formed on the base film by vacuum deposition. Examples of sealable top coatings disclosed are polyethylene and vinylidene chloride/acrylonitrile copolymer.

SiO is known to have better barrier properties than SiO<sub>2</sub>, but unfortunately SiO is much more expensive than SiO<sub>2</sub> and imparts a yellow color to the package in the coating thickness required for development of its good barrier properties.

Nevertheless, after all the years since publication of U.S. Patent 3,442,686 in 1969, a commercial product has finally been introduced (in Japan) in which the glassy coating is a layer of SiO sandwiched between two layers of polyethylene terephthalate (PET) film and a cast polyolefin top coating to form a packaging film. For one of the products, the SiO layer thickness is on the order of 2000 Angstroms (200 nm). Another product consists of a laminate in which two superimposed layers of SiO are present, each having a thickness of 1200 Angstroms (120 nm), giving a total effective SiO thickness of 2400 Angstroms (240 nm). These products have two disadvantages. First the product has a distinctly yellow color arising from the SiO layer(s) at the layer thicknesses involved, i.e., SiO has a yellow color, which becomes more intense as its thickness increases. It is believed that the yellow color of the SiO coating is somewhat ameliorated by carrying out the vapor deposition of the coating in the presence of oxygen, whereby the SiO is on the order of SiO<sub>1.5</sub>. Second, the packaging film constituting this commercial product has the disadvantage of high cost arising from the high thickness and high relative cost of SiO present in the packaging film to provide the needed barrier properties. To their credit, however, these packaging films are reported to be able to survive retorting at 125°C without loss of barrier property.

Effort has been made to use SiO<sub>2</sub> coating instead of SiO for economy reasons and in order to obtain a colorless package. To some extent, the barrier properties of SiO<sub>2</sub> can be improved by increased thickness, but there is a limit to this approach because of decreasing flexibility with increasing thickness.

U.S. Patent 4,702,963 discloses packaging film in which an adhesion layer is first vacuum deposited on a flexible polymer substrate, followed by vacuum deposition of a barrier layer, to confer retortability to the packaging film. The adhesion layer can consist of Cr, which is preferred, co-deposited mixtures of Cr and SiO having at least 20% by weight Cr, among others. The barrier layer is preferably silicon monoxide or silicon dioxide. When silicon dioxide is used, it may be mixed with glass modifiers such as oxides of Mg, Ba, and Ca, or with fluoride of alkaline earth metals, e.g. MgF<sub>2</sub>. The glass modifiers serve to alter the color appearance of the overall coating. For example, a chromium/SiO composite film is disclosed to produce a coating with a yellowish appearance, while a neutral gray appearance is disclosed to result from the mixture of SiO<sub>2</sub> with glass modifiers. The specific adhesion/barrier layer systems disclosed in the Examples are primarily chromium as the adhesive layer and SiO or SiO<sub>2</sub> as the barrier layer. The lead-alumina silica glass is used as an adhesive layer, as is Ta-Cr alloy, Ta, Mo, and chromium oxides. In some Examples, the SiO<sub>2</sub> layer is mixed with a modifier. In Table 4,

chromium, cobalt, copper, indium, iron, lead, manganese, tin, titanium, tungsten, zinc, and zirconium, wherein the amount of said glassy coating and the amount of metal contained therein is suitable to provide an oxygen transmission value through said film structure of at most about 5 mL/day-m<sup>2</sup>-atm.

In another embodiment of the present invention, a multilayer structure comprises the resin substrate of polyester or polyamide with sequentially vacuum deposited thin and thicker SiO and SiO<sub>2</sub> layers, respectively, thereon. Preferably, the thickness of the SiO layer on the substrate is about 10 to 75 nm (about 100 to 750 Angstroms) and of the SiO<sub>2</sub> layer deposited on the SiO layer is at least about 20 nm (200 Angstroms), with the thicknesses of these layers being selected to provide the barrier properties desired. The SiO layer at these small thicknesses provides virtually no barrier properties and yellow coloration is either barely perceptible or not perceptible at all. For many of the thicknesses of SiO<sub>2</sub> except at the higher thicknesses virtually no significant barrier properties are present. Together, however, these layers provide barrier properties better than the sum of the individual layers.

In still another embodiment of the present invention, the foregoing-described SiO<sub>2</sub> layer of the preceding embodiment incorporates a dopant selected from a wide variety of metallic materials which have the effect of improving the retortability of the multilayer structure as measured by barrier properties, instead of by a simulated retortability test involving only adhesion testing. The dopant improves the pre-retort barrier properties of the SiO<sub>2</sub> layer if no SiO underlayer were present as in the first mentioned embodiment. In the present invention, however, wherein the SiO underlayer is present, the dopant does not appear to appreciably affect pre-retort barrier properties. Instead, the presence of the dopant used in accordance with this embodiment of the present invention tends to stabilize these properties so that they carry over into the retorted multilayer structure.

Another embodiment of the present invention is the process for making a barrier structure from polyester or polyamide polymer as the resin substrate by carrying out the sequential vacuum deposition to form the SiO and SiO<sub>2</sub> combination of layers described above.

The present invention further provides a similar structure and process in which the dopant is lithium borate.

#### Description of the Drawing

The drawing is directed to the embodiments of the present invention involving the combination of SiO and SiO<sub>2</sub> layers. The drawing is a schematic cross section of a length of multilayer structure 2 of the present invention, comprising a resin substrate 4 having a layer 6 of SiO vacuum deposited thereon, and a layer 8 of SiO<sub>2</sub> vacuum deposited in the SiO layer. Preferably, for this embodiment, a protective outer layer 10 of adherent plastic resin is present in the multilayer structure.

#### DETAILED DESCRIPTION OF THE INVENTION

The barrier films of the present inventions are polymeric substrates such as films, coated directly or indirectly with specially selected glass coatings. The polymeric substrates include any having suitable physical and thermal properties for the particular packaging application at hand. The minimum requirement is that they have sufficient thermal and physical properties to withstand the conditions of application of the glass coating, described in more detail below, and exhibit sufficient adhesion to the glass coating. Examples of suitable substrates for use when the SiO<sub>2</sub> is coated directly onto the polymeric substrate include those prepared from polyamides, including amorphous and semicrystalline polyamides, polyethers, polyketones, polyester ethers, and polyesters (including polycarbonates), which are preferred. When it is SiO that is directly coated onto the polymeric substrate, the substrate is selected so as to be compatible with the SiO layer so that it can withstand retorting and provide the desired barrier properties. Polymeric substrates of polyester or polyamide provide this compatibility.

Examples of polyester resins include polyethylene naphthalate, polycarbonate, and polyarylate, and most preferably polyethylene terephthalate ("PET"). Examples of semicrystalline polyamides include polycaprolactam (nylon 6) and condensation polymers of dicarboxylic acids and diamines, such as polyhexamethylene adipamide (nylon 6,6) etc. Examples of amorphous polyamides include hexamethylenediamine isophthalamide, hexamethylenediamine isophthalamide/terephthalamide terpolymer, having iso/terephthalic moiety ratios of 100/0 to 60/40, mixtures of 2,2,4- and 2,4,4-trimethylhexamethylenediamine terephthalamide, copolymers of hexamethylene diamine and 2-methylpentamethylenediamine with iso- or terephthalic acids, or mixtures of these acids. Polyamides based on hexamethylenediamine iso/terephthalamide containing high levels of terephthalic acid moiety may also be useful particularly when a second diamine such as 2-methyl-diaminopentane is incorporated to produce a processible amorphous polymer. Typically a substrate, especially a film, will have been oriented, optionally followed by heat setting so as to provide dimensional and thermal stability.

the vacuum deposition process. A source of silicon dioxide and dopant metal (either in different sources or combined in a single source, either as a powder, a metal wire, or vitrified into a silica glass) is placed in the vacuum chamber and vaporized by heating with an electron beam or a resistance or induction heated furnace, or by sputtering or reactive sputtering by an ion beam or a magnetron source, or the like. The silicon dioxide, along with the dopant metal, condenses to form the desired coating.

The dopant can be incorporated into the  $\text{SiO}_2$  layer either by evaporating a single source of a physical or fused mixture of the dopant and  $\text{SiO}_2$ , or by co-depositing the dopant and the  $\text{SiO}_2$  from two or more sources simultaneously. In both cases, the dopant can be in a metallic form or in the form of an oxide, silicide, silicate, halide, or carbonate, and the like. In the case of depositing from a single source, the proportion of the dopant present in the deposited  $\text{SiO}_2$  layer may vary from the composition of the source. Such proportion can be determined for a particular source composition and conditions of vacuum deposition and can be adjusted to the proportion desired by adjustment of the source composition. In case of either deposition method, the composition of the coating can be determined by analysis of atomic absorption using inductively coupled plasma (ICP), which is a conventional analysis procedure. This analysis primarily detects the elemental metal in the  $\text{SiO}_2$ . Therefore, the weight percents of dopant disclosed herein are based on the elemental metal of the metal dopant. Thus decomposition products, e.g.  $\text{CO}_2$  from carbonates, which do not become part of the  $\text{SiO}_2$  layer are not included in weight percents of dopant in that layer. The weight percents of dopant disclosed herein refer to the composition of the  $\text{SiO}_2$  layer unless otherwise indicated. These same weight percents may, however, be present in the source(s) for vacuum deposition (co-deposition), and as previously described, the resultant composition of the  $\text{SiO}_2$  layer for the vacuum deposition conditions used can then be determined, and the source composition can be adjusted in subsequent runs to obtain the final composition desired. More often, the source composition will be adjusted to provide the barrier properties desired for the multilayer structure rather than analyzing the  $\text{SiO}_2$  layer for its dopant content.

The silicon dioxide coating of the present invention is "doped," as described above, with a high level of at least one of a select group of metals. The term "doping" is used herein to describe a deposition with silicon dioxide of a relatively high level of metal, typically 0.5 to about 25 weight percent, as measured in the source, or about 0.5 to about 30 weight percent as measured as metal in the glass coating itself.

The oxidation state of the metal as it resides in the coating matrix of silicon dioxide is not necessarily clearly understood or well defined. Thus if an elemental metal is used as the source for the dopant, the deposited metal atoms or particles may interact with the oxygen atoms of the matrix to form a partially or completely oxidized material. Alternatively, if an oxide of the metal is used as the source, it is not necessarily known nor is it necessarily important whether the metal is deposited into the glassy matrix as the oxide or as the elemental metal. It appears that either the elemental metal or an oxide of the metal or certain other metal compounds, regardless of oxidation state can be suitably used as the source of the dopant metal for the present invention. Such possibilities and equivalents thereof are included within the scope of the present invention when terms such as "metal dopant" or the like are used. The selection of an appropriate source for metal dopant will be within the abilities of one skilled in the art and will be determined by such factors as relative cost and ease of handling. In many cases the metal oxide or especially the elemental metal will be preferred.

Suitable metal dopants for the present invention include antimony, aluminum, chromium, cobalt, copper, indium, iron, lead, manganese, tin, titanium, tungsten, zinc, and zirconium. Preferred metals include chromium, manganese, zinc, and most preferably copper and tin. When one or more of these metals are present, the barrier property of the glass coating and of the structure as a whole is greatly improved. Surprisingly it has been found that many other metals do not show this sort of improvement. Among the metals that are not particularly effective at comparable levels are calcium, vanadium, lithium, nickel, molybdenum, gold, germanium, and selenium. Sulfur is similarly not effective. It is surprising that these elements appear in the same regions of the periodic table with the metals that are effective. The chemical phenomenon that distinguishes between these groups of metals is not understood. It is noted that the metals which form a part of the present invention are generally located to the right of Column II of the Periodic Table, that is, to the right of the alkali metals and the alkaline earth metals.

When a metal dopant from the metals of the present invention is used in the layer of silicon dioxide, the improvement in barrier properties can be dramatic. One customary measurement of barrier properties of a film is its oxygen transmission rate ("OTR", ASTM D-3985-81(1988)) expressed as mL oxygen passage/m<sup>2</sup>-day-atmosphere. A film of ordinary untreated PET, 23 micrometers thick, typically has an OTR of 75-90; that of a 12 micrometer film is typically 150-180. Addition of a 300 nm coating of  $\text{SiO}_2$  reduces the OTR somewhat, to about 10-80. Addition of one or more of the metals of the present invention can routinely reduce the OTR to less than 5. In copper, the most preferred case, addition of even 1 percent to the  $\text{SiO}_2$  (measured in the source) can reduce the OTR to as low as 0.5, while use of 5-10 percent copper can result in values as low as 0.3. Use of tin, which is also preferred, provides values nearly as low.

structures of the present invention are high, preferably not appreciably degrading the light transmission of the resin substrate. The  $\text{SiO}_2$  layer, even containing metallic material dopant can be and is preferably colorless, so that the entire multilayer structure is colorless.

As previously stated herein, the metal dopant appears to have the effect of enabling the barrier properties of the multilayer structure to survive retorting, e.g. prolonged contact with boiling water under pressure at temperatures at least  $125^\circ\text{C}$ .

One measure of improved barrier properties is reduced oxygen transmission through the multilayer structure.

Multilayer structures of this embodiment of the present invention can achieve barrier properties characterized by an oxygen transmission rate (OTR) of less than about  $7 \text{ ml/m}^2 \text{ Day Atm}$ , preferably before and after retorting. The preferred oxygen transmission rate before and after retorting is less than about  $3 \text{ ml/m}^2 \text{ Day Atm}$ . The oxygen transmission is measured on a Model "OX-TRAN 1000" made by Modern Controls Inc. of Minneapolis MN in accordance with ASTM test D 3985-81 (1988) except that the test is carried out at  $30^\circ\text{C}$  and at 80% relative humidity, using 100% (1 Atm pressure) oxygen, with the result being normalized to  $1 \text{ m}^2$  of multilayer structure and one day's duration for the test. The retorting procedure used for these tests involves placing the multilayer structure in a bath of water in an autoclave under 2.5 Atm absolute pressure at  $125^\circ\text{C}$  for 30 minutes in addition to the time for heating up (30 minutes) and cooling down (15 minutes) the water bath in which the multilayer structure is immersed.

The other barrier property of primary interest in food packaging is the barrier to water vapor. Multilayer structures of this embodiment of the present invention also exhibit low permeability to passage of water vapor, both before and after retorting. Preferably, the water vapor transmission of multilayer structures of the present invention is no greater than about  $5 \text{ g/m}^2$  from 90% relative humidity to 50% relative humidity, and more preferably no greater than about  $3 \text{ g/m}^2$  (same relative humidity conditions) as measured by ASTM-F 1249.

In all embodiments of the present invention, an additional protective layer for the  $\text{SiO}_2$  layer can be added (with or without dopant). Such a layer can be selected from any plastic resin that adheres to the  $\text{SiO}_2$  layer or that adheres via an intervening adhesive layer. Examples of protective layers include a layer of polyester (adhered to the  $\text{SiO}_2$  layer via an adhesive), polyamides, acrylonitrile copolymers, polyvinylidene chloride, polyethylene, polypropylene, ethylene vinyl acetate copolymer, ethylene/acrylic or methacrylic acid copolymer and ionomer. The protective layer can be applied to the  $\text{SiO}_2$  layer by conventional processes such as adhesive or thermal laminating or extrusion coating simultaneous with extrusion of the intervening adhesive, if any. The protective layer can also be provided by solvent or dispersion coating onto the  $\text{SiO}_2$  layer, using multiple coatings if thickness greater than achievable by single coating is desired. The thickness of the protective layer will generally be about 0.5 to 100 micrometers, preferably 10 to 25 micrometers (0.010 to 0.025 mm). In one embodiment, the protective layer is biaxially oriented PET film (0.0234 mm thick), which is laminated to the exposed surface of the  $\text{SiO}_2$  layer via a co-polyester adhesive resin available as Adcote 506-40 ( $2.7 \text{ g/m}^2$ ) from Morton Chemicals and a nip roll heated at  $120^\circ\text{C}$  for pressing the film and laminate structure against one another.

Films and structures of the present invention are useful as a wide variety of packaging, from rigid to semi-rigid containers to packaging film where barrier properties towards oxygen and other materials are desired. The particular use will dictate the choice and shape of the resin substrate. For packaging films, the resin substrate will be in the form of a film having, for example, a thickness of 10 to 150 micrometers, often 12 to 50 or preferably 15 to 25 micrometers. The high light transmission and colorless appearance of packaging of multilayer structures, especially those which contain the  $\text{SiO}/\text{SiO}_2$  combination of layers serves as a good showcase for food packaged therein, and the high barrier properties of such packaging provides excellent preservation of this food.

Examples of the present invention are as follows (parts and percents are by weight unless otherwise indicated):

#### Examples 1-136

Silicon dioxide was mixed with a dopant material and loaded into the hearth (crucible) of an electron beam evaporator of the single crucible bent beam source type as sold by a variety of manufacturers including Denton Vacuum of Cherry Hill, NJ. A thin film was formed from this mixture onto the smoother surface of a 23 micrometer (92 gauge) PET film (Mylar® type D) by electron beam evaporation from the mixture. The accelerator voltage was continuously adjusted to sweep the beam across the material in the source crucible to give uniform erosion of the crucible's contents. The filament current (and hence the beam current) was adjusted to provide a high deposition rate, resulting in a relatively high background pressure of about  $1.3 \times 10^{-2} \text{ Pa}$  (about  $1 \times 10^{-4} \text{ torr}$ ). This pressure was not so high as to cause premature arc-over of the electron beam gun. The thickness of the deposit was monitored by a calibrated oscillating quartz crystal monitor such as manufactured by Veeco Instruments Inc., Plainview, NY. The film (unless another grade is reported) had an average (RA) surface roughness

TABLE II

Ex.	Dopant, %	Thickness, nm	OTR	OPV X 10 <sup>6</sup>
C12	Ag	10	301	8.5 2944
C13	AgO	10	300	5.9 1944
C14	BaO	10	307	2.6 828
C15	"	30	315	7.7 2743
C16	B <sub>2</sub> O <sub>3</sub>	3	326	80.3 >100000
C17	"	10	213	77.2 >100000
C18	"	10	327	83.4 >100000
C19	Ca(BO <sub>2</sub> ) <sub>2</sub>	10	290	74.7 >100000
C20	"	10	303	35.5 23832
C21	"	25	239	82.5 >100000
C22	"	50	230	73.2 >100000
C23	CaO	10	301	6.0 1985
C24	"	30	265	12.3 4042
C25	K <sub>2</sub> O	10	308	27.0 14319
C26	Li	3	--	80.6 --
C27	Li <sub>2</sub> B <sub>4</sub> O <sub>7</sub>	1	307	2.5 797
C28	"	2	301	2.4 756
C29	"	7	301	41.5 34897
C30	LiF	1	301	30.1 17002
C31	"	4	300	50.4 68597
C32	MgCl <sub>2</sub>	2	301	51.7 78306
C33	"	10	246	19.0 6639
C34	"	10	246	23.3 8955
C35	MgF <sub>2</sub>	1	303	20.6 9185
C36	"	2	299	1.1 320
C37	"	5	105	4.0 449
C38	"	5	201	2.2 455
C39	"	5	303	1.1 334
C40	"	10	297	1.1 328
C41	"	10	308	1.1 340
C42	"	15	306	2.2 713
C43	"	30	--	10.2 --
C44	MgO	5	304	1.9 602
C45	"	10	302	5.4 1766
C46	"	35	215	1.6 341
C47	"	35	306	1.6 486
C48	Na <sub>2</sub> B <sub>4</sub> O <sub>7</sub>	4	321	29.9 17889
C49	"	10	--	57.2 --
C50	"	10	265	66.0 >100000
C51	Na <sub>2</sub> SO <sub>4</sub>	5	302	60.2 >100000
C52	"	20	304	70.3 >100000

TABLE IV

	Ex.	Dopant, %	Thickness, nm	OTR	OPV X 10 <sup>6</sup>
5	68	Al	2 303	1.9	595
	69	"	10 303	1.3	403
	70	"	10 311	1.6	494
	71	"	15 312	4.5	1496
10	C72a	"	30 321	14.3	5875
	73	Co	10 214	0.9	196
	74	Cr	10 303	1.3	408
	75	"	20 302	1.9	603
15	76	"	30 300	0.7	207
	77	"	30 302	1.3	387
	C78	Cu	1 300	8.1	2793
	C79a	"	1 300	124.0	>100000
20	80	"	1 301	0.5	160
	81	"	2 26	3.7	102
	82	"	2 52	4.9	276
	83	"	2 301	0.7	198
	84	"	3 303	4.1	1334
25	85b	"	5 ---	0.7	---
	C86	"	5 28	11.4	388
	87	"	5 51	2.1	109
	88	"	5 100	0.9	90
	89	"	5 301	0.5	160
30	90	"	5 301	1.0	308
	91	"	5 303	0.3	80
	92c	"	5 305	2.6	829
	93d	"	5 300	2.5	770
	94e	"	5 295	2.2	658
35	C95f	"	5 300	7.6	2428
	96g	"	5 298	5.1	1712
	97h	"	5 300	0.9	271
	98h	"	5 302	1.8	567
	99i	"	5 301	1.5	527
40	100	"	5 301	0.9	289
	C101	"	5 303	60.3	>100000
	C102	"	10 26	7.6	225
	103	"	10 28	2.9	84
	104	"	10 51	2.9	155
45	105	"	10 102	3.3	360
	106	"	10 117	2.1	257
	107	"	10 301	0.3	94
	108	"	10 301	0.5	155
	109	"	15 100	1.3	136
50	110	"	20 301	2.3	726
	111	"	30 300	0.6	188

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acid, then dissolved by addition of concentrated nitric acid (aqua regia) and concentrated hydrofluoric acid and heating. The solution is diluted to 100 mL and analyzed by an Applied Research Laboratories 34000 simultaneous inductively coupled plasma analyzer or a Perkin Elmer 6500 (sequential) inductively coupled plasma analyzer. The amounts of the reported elements are calculated assuming that the dopant is the elemental metal and the matrix is  $\text{SiO}_2$  (m.w. 60). The results are shown in Table V.

Table V  
Thickness

	Ex.	Dopant	Thickness (nm)	Source %	Coating %
10	C137	Ag	303	10.0	0.1
	C138	$\text{B}_2\text{O}_3$	300	10.0	0.7
	C139	$\text{MgF}_2$	302	5.0	0.6
	C140	"	301	10.0	1.0
15	C141	Mo	301	10.0	13.4
	C142	$\text{Na}_2\text{B}_7\text{O}_{14}$	302	10.0	(2.1 Na) (1.3 B)
	C143	Ni	300	10.0	16.3
20	144	Al	302	5.0	3.8
	145	"	312	10.0	4.0
	146	"	303	10.0	<1.8
	147	Fe	298	5.0	7.4
25	148	"	304	10.0	13.5
	149	Cr	301	2.0	3.2
	150	"	301	5.0	8.8
	151	"	298	5.0	7.7
30	152	"	304	10.0	14.6
	153	"	301	10.0	14.1
	154	Cu	147	5.0	10.5
	155	"	299	5.0	0.0
35	156	"	300	5.0	1.5
	157	"	307	5.0	8.7
	158	"	310	5.0	7.4
	159	"	152	10.0	15.8
	160	"	299	10.0	8.7
40	161	"	303	10.0	6.2
	162	"	305	10.0	21.2
	163	"	276	10.0	17.1
	164	"	301	20.0	30.2
	165	"	153	20.0	29.8
45	166	Mn	302	10.0	12.9
	167	Sn	301	2.0	8.8
	168	"	152	5.0	12.2
	169	"	304	5.0	24.3
50	170	"	302	5.0	17.5
	171	"	301	5.0	12.0
	172	"	271	5.0	8.8
	173	"	153	10.0	14.6
	174	"	306	10.0	24.7
55	175	"	285	10.0	26.4

The considerable scatter in the analysis of the coating composition is believed to arise from several sources



Table VI

Ex.	Dopant, %	Thickness (nm)	% Transmission	
			400 nm	550 nm
5 C176	(no coating)		85.01	88.71
C177a	(no coating)		69.25	77.34
C178	none	--	81.85	83.18
C179	"	303	75.68	83.56
10 C180	MgF <sub>2</sub>	5	88.10	88.10
181	"	5	88.98	90.19
182	"	10	86.90	92.17
C183b	SF <sub>6</sub>	5	86.60	87.70
15 184	Al	5	76.21	80.91
185	"	15	38.90	75.86
186	"	30	1.45	28.18
20 187	Cr	5	84.96	88.73
188	"	10	82.45	82.42
189	"	10	85.62	90.07
190	"	20	81.16	83.67
191	"	20	70.89	78.76
25 192	"	20	12.30	31.62
193	Cu	5	59.57	71.94
194	"	5	73.79	81.66
195	"	10	64.12	72.44
30 196	"	10	51.71	71.94
197	"	20	84.96	88.73
198	"	20	50.05	61.44
199	"	20	25.59	39.81
200	"	20	53.48	65.80
35 201	Fe	5	87.90	89.41
202	"	10	82.99	89.54
203	Mn	10	78.16	83.95
40 204	Pb	10	26.61	41.88
205	Sn	5	85.11	88.72
206	"	10	82.70	85.51
45 207	"	10	84.45	85.29
208	"	20	86.50	90.16
209	"	20	25.94	36.31

a. Commodity PET film with internal slip additive, 24 micrometers thick.

b. Coating prepared from lead glass - about 70% Pb.

#### Example 210

This Example demonstrates the improvement provided by the SiO/SiO<sub>2</sub> multilayer combination in terms of barrier properties.

Example 211

A multilayer film structure of a layer of 31 nm thickness of SiO on the PET film used in Example 210 and a layer of 202 nm thickness of SiO<sub>2</sub> on the SiO layer was prepared in the same manner as Example 210 and the resultant colorless barrier film was subjected to retorting by placement in a bath of water in an autoclave at 125°C for 30 minutes. While the film was unchanged in visual appearance to the naked eye, the OTR of the film degraded to 39.8 ml/m<sup>2</sup> day Atm, suggesting that this combination should be used where the film structure would not be subjected to retorting, e.g., for packaging tea, coffee, cereals, and cigars.

Example 212

This example shows the effect of varying the stoichiometric ratio of oxygen to silicon in the SiO underlayer formed on the PET film. The multilayer structure: PET film/SiO/SiO<sub>2</sub>, by the procedure of Example 210, using the PET film used in that Example, with the following results:

Table VIII

	SiO	SiO <sub>2</sub>	OTR
	Layer thick-	Layer thick-	(after retort)
	ness (nm)	ness (nm)	(ml/m <sup>2</sup> Day Atm)
Ratio of O:Si			
1.25:1	54	283	0.9
1.5:1	31	240	>150

In the experiments addressed in Table VIII, the SiO<sub>2</sub> layer was doped with Sn by vacuum deposition by electron beam evaporation of a 95/5 weight source mixture of SiO<sub>2</sub> and Sn. The SiO layer was formed to contain the greater proportion of oxygen as indicated in Table VIII by mixing SiO and SiO<sub>2</sub> together in the weight ratio indicated to form a single source (target). The permeability testing was carried out after retorting of the film structure by the procedure described in Example 211. From these results it can be seen that as the oxygen ratio increases in the SiO underlayer, the retortability of the multilayer structure decreases.

Example 213

This Example shows the effect of SiO layer thickness on barrier properties for PET film/SiO/SiO<sub>2</sub> multilayer film structure by the procedure of Example 210, using the PET film used in that Example, with the following results:

Table IX

SiO layer	SiO <sub>2</sub> layer	OTR (after retort)
thickness nm	thickness	(ml/m <sup>2</sup> Day Atm)
2	238	81.0
5	241	84.9

The SiO<sub>2</sub> layer in this Example was doped with 5% Sn in the same manner as reported for Table VIII and the oxygen permeability was determined after the film structure had been retorted as described in Example 211. This retorting virtually destroyed the barrier property of the film structure whereas for the thicker SiO layer used in the first experiment of Table VIII, excellent barrier property was exhibited after retorting even though the SiO layer was somewhat diluted by its 1.25:1 O<sub>2</sub> to Si ratio.

Example 214

In this example, the film structure PET film/ 13 nm SiO/308 nm SiO<sub>2</sub>+5% Cu (source mixture) was prepared and tested for oxygen permeability by the same procedure as Example 210, but after retorting by the procedure of Example 211, and the resultant OTR was 2.8 ml/m<sup>2</sup> day Atm indicating that a moderately thin SiO layer serves

Example 219

A number of barrier films of the structure PET film/SiO/SiO<sub>2</sub> were formed by vacuum deposition by the procedure of Example 210, in which the PET film was Mylar D and the SiO<sub>2</sub> layer contained various dopants (source compositions reported based on the elemental metal of the dopant), and on which OTR values were obtained either before or after retorting in accordance with Example 211. The results are shown in Table X.

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For experiment k., the PbO was supplied in the form of a fused glass designated SF-6 available from Schott Glass Technologies, Inc. Duryea, PA. and contained a small proportion of SiO<sub>2</sub>.

Comparison of experiments a. with b. and c. with d. show stabilizing effect of the dopants in the amounts used on oxygen permeability before and after retorting. The element In was less effective in the amount used, but the result after retorting was still more than 10 times better than the PET film by itself.

Mn as the dopant in experiment g. produced a barrier film with a useful oxygen impermeability after retorting, while the OTR value for experiment h. suggests that too much Mn was present in the SiO<sub>2</sub> layer.

Experiments j. through m. all gave barrier layers with useful oxygen impermeabilities.

#### Example 220

In this Example, The SiO underlayer was replaced by an SiO<sub>2</sub> layer to yield the following multilayer film structure: PET film/32 nm SiO<sub>2</sub>/271 nm SiO<sub>2</sub> + 5% Cu (source compositions). The PET film was Mylar D. The vacuum deposition procedure of Example 210 was used and the retort procedure of Example 211 was used. The OTR of this structure after retorting was 92.5 ml/m<sup>2</sup> Day Atm. The structure was clear and transparent, giving no visual evidence that the oxygen barrier had failed. In addition, the SiO<sub>2</sub> layers were strongly adhered to the PET film as indicated by a peel strength of 144.5 g/cm exhibited by a nearly identical film structure.

#### Example 221

This Example shows the high transparency and low water vapor transmission of a number of multilayer structures of the present invention prepared by the procedure of Example 210 using the PET film of that Example as the resin substrate, details of these structures and light transmissions being reported in Table XI (light transmission) and Table XII (water vapor transmission).

Table XII  
Visible Light Transmission

SiO Layer thickness(nm)	SiO <sub>2</sub> Layer thickness(nm)	dopant(wt%)	% Light Transmission	
			400 nm	550 nm
24	271	5 Cu	72.06	88.24
25	125	5 Sn	77.61	87.36
50	252	5 Sn	77.33	78.28
32	270	10 Cr	77.74	89.85
30	272	10 Fe	69.02	77.16
57	254	5 In	75.60	88.47
30	273	5 Mn	73.66	80.17

These light transmissions compare favorably with the light transmission of the PET film used as the resin substrate, which by itself exhibited light transmissions of about 86% (400 nm) and almost 92% (550 nm) and especially favorably with the light transmissions of PET commodity packaging film, viz, about 69% (400 nm) and about 78% (550 nm). The transmission of the Sn, Fe, and Mn containing structures were measured after retorting by the procedure of Example 211.

8. The structure of any one of claims 1 to 7 wherein the amount of dopant metal calculated as elemental metal is about 0.5 to about 30 weight percent of the glassy coating.
9. The structure of any one of claims 1 to 8 wherein the polymeric substrate has a surface smoothness such that the average height of roughness is less than about 50 nanometers.
10. The structure of any one of claims 1 to 9 wherein the polymeric substrate is a film of polyester or polyamide.
11. The structure of claim 10 wherein the polyester is oriented polyethylene terephthalate.
12. The structure of any one of Claims 1 to 11 wherein a layer of SiO is present between said polymeric substrate and said coating of silicon dioxide.
13. A structure having superior barrier properties, comprising:
  - (a) a polymeric substrate, and
  - (b) a glassy coating of silicon dioxide doped with lithium borate in an amount suitable to provide an oxygen transmission value through the coated structure of at most about 5 mL/day-m<sup>2</sup>-atm.
14. A process for imparting barrier properties to a polymeric substrate, comprising the steps of:
  - (a) selecting a polymeric substrate; and
  - (b) vacuum depositing directly or indirectly onto said polymeric substrate a glassy coating derived from silicon dioxide and at least one metal selected from the group consisting of antimony, aluminum, chromium, cobalt, copper, indium, iron, lead, manganese, tin, titanium, tungsten, zinc, and zirconium; wherein the amount of said glassy coating and the amount of metal contained therein is suitable to provide an oxygen transmission value of at most about 5 mL/day-m<sup>2</sup>-atm.
15. A multilayer structure comprising a polymeric substrate of polyester or polyamide, a vacuum deposited layer of SiO of about 10 to 75 nm thickness on said substrate, and a vacuum deposited layer of SiO<sub>2</sub> of at least about 20 nm thickness on said SiO layer.
16. The multilayer structure of Claim 15 wherein said SiO layer has an atomic ratio of oxygen to silicon in said layer of from 0.6:1 to 1.4:1.
17. The multilayer structure of Claim 15 or 16 wherein said SiO<sub>2</sub> layer contains an effective amount of dopant to improve its barrier properties upon retorting of said multilayer structure.
18. The multilayer structure of Claim 17 wherein said dopant is a metallic material selected from the group consisting of Ti, Zr, Zn, Al, In, Pb, W, Cu, Sn, Cr, Fe, Mn, Sb, Co, Ba, and Mg, and mixtures thereof, and the amount thereof present in said SiO<sub>2</sub> layer is about 0.5 to 30% based on the total weight of the layer.
19. The multilayer structure of any one of Claims 15 to 18 having an oxygen transmission rate (OTR) of less than about 7 cc/m<sup>2</sup> Day Atm.
20. The multilayer structure of Claim 19 wherein said oxygen transmission rate is present both before and after retorting.
21. The multilayer structure of any one of Claims 15 to 20 in the form of a film.
22. The multilayer structure of any one of Claims 15 to 20 in the form of a container.
23. A process for forming a barrier structure from a resin substrate of polyester or polyamide polymer comprising vacuum depositing a layer of SiO of about 10 to 75 nm thickness on said container and vacuum depositing a layer of SiO<sub>2</sub> of at least about 20 nm thickness on said SiO layer, the resultant multilayer structure having an oxygen transmission rate (OTR) of less than about 7 cc/m<sup>2</sup> Day Atm.
24. The process of Claim 23 wherein metal dopant is vacuum deposited along with the vacuum deposition of said layer of SiO<sub>2</sub> so that said metal dopant is incorporated in said SiO<sub>2</sub> layer in effective amount to provide said OTR after retorting of said structure.